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Spin-orbit holds the heavyweight title for Pu and Am: Exchange regains it for Cm

Kevin Moore, Gerrit van der Laan, Per Soderlind

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Dijon, France
July 7, 2008 through July 11, 2008

Disclaimer

Competition between spin-orbit and exchange interaction in Pu, Am, and Cm: *What Cm has taught us about magnetism and the crystal structure of metals*

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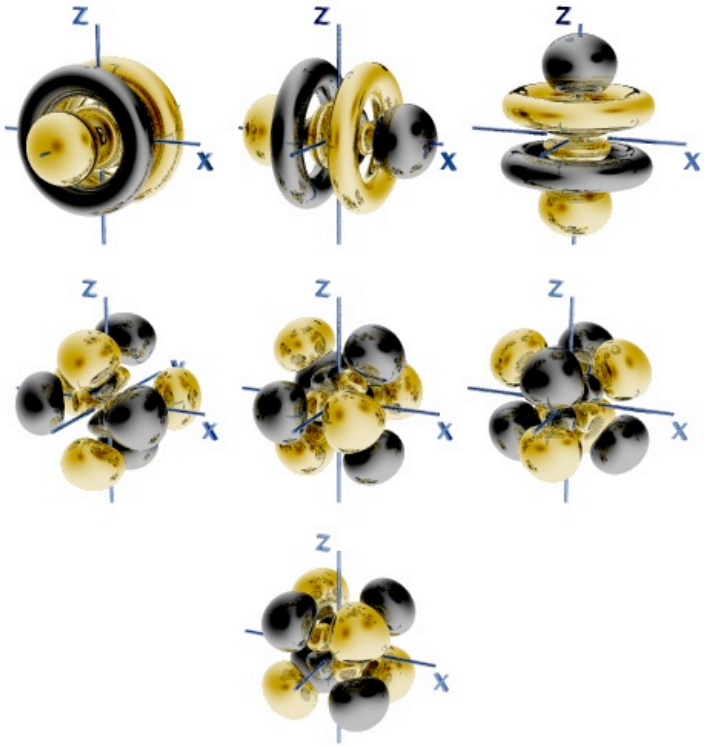

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Curium: Obscure, but incredibly interesting!

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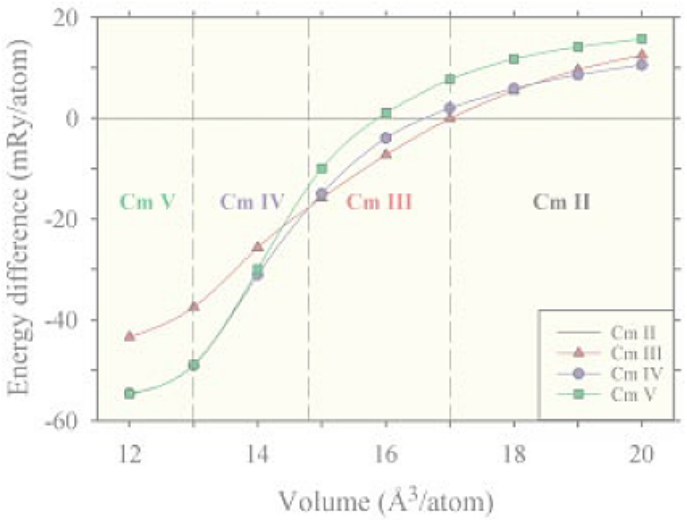
A High-Pressure Structure in Curium Linked to Magnetism

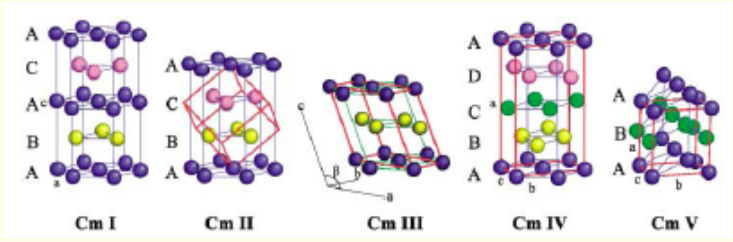
S. Heathman,[1]* R. G. Haire,[2] T. Le Bihan,[3]† A. Lindbaum,[4] M. Idiri,[1] P. Normile,[1] S. Li,[5,6] R. Ahuja,[5,6] B. Johansson,[5,6] G. H. Lander[1]

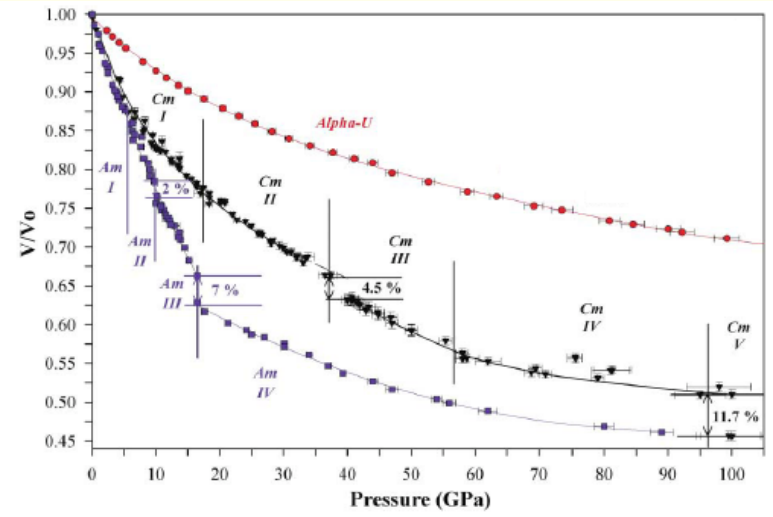
Curium lies at the center of the actinide series and has a half-filled shell with seven 5*f* electrons spatially residing inside its radon core. As a function of pressure, curium exhibits five different crystallographic phases up to 100 gigapascals, of which all but one are also found in the preceding element, americium. We describe here a structure in curium, Cm III, with monoclinic symmetry, space group *C2/c*, found at intermediate pressures (between 37 and 56 gigapascals). Ab initio electronic structure calculations agree with the observed sequence of structures and establish that it is the spin polarization of curium's 5*f* electrons that stabilizes Cm III. The results reveal that curium is one of a few elements that has a lattice structure stabilized by magnetism.

Science **309**, 2005.



What causes magnetic stabilization of Cm?





U stays the same phase from 0 - 100 GPa while Am and Cm undergo several phase transformations with volume collapses.

Curium: Obscure, but incredibly interesting!

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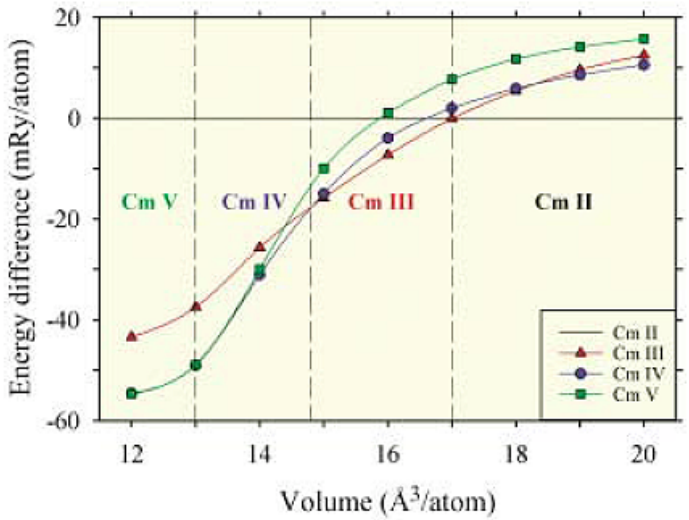

Questions:

What is the underlying physical reason the monoclinic crystal structure of Cm III is stabilized by it's own *intrinsic* magnetism?

What does the answer tell us about magnetic stabilization of crystal structures throughout the Periodic Table?

DFT calculations show that spin polarization is needed to get the correct phases.

Cm III can ***only*** be stabilized with spin polarization, meaning the phase is stabilized by magnetism.

Angular-momentum coupling of electrons: How they fill the bonding states

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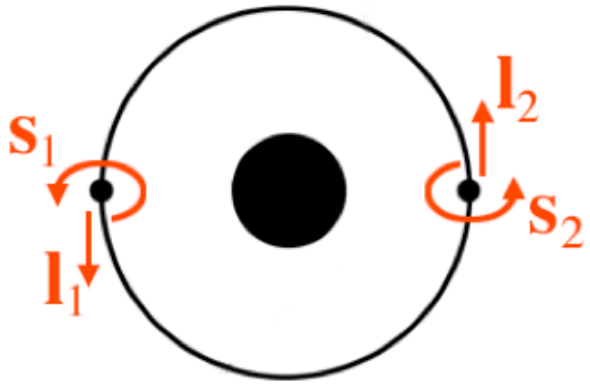
Russell-Saunders (*LS*)

spin-spin > orbit-orbit > spin-orbit

jj

spin-spin < orbit-orbit < spin-orbit



For two particles (1,2) and 4 angular momenta (l_1, l_2, s_1, s_2)

LS	*jj*
$L = l_1 + l_2$	$j_1 = l_1 + s_1$
$S = s_1 + s_2$	$j_2 = l_2 + s_2$
$J = L + S$	$J = j_1 + j_2$

Angular-momentum coupling of electrons: How they fill the bonding states

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Russell-Saunders (*LS*)

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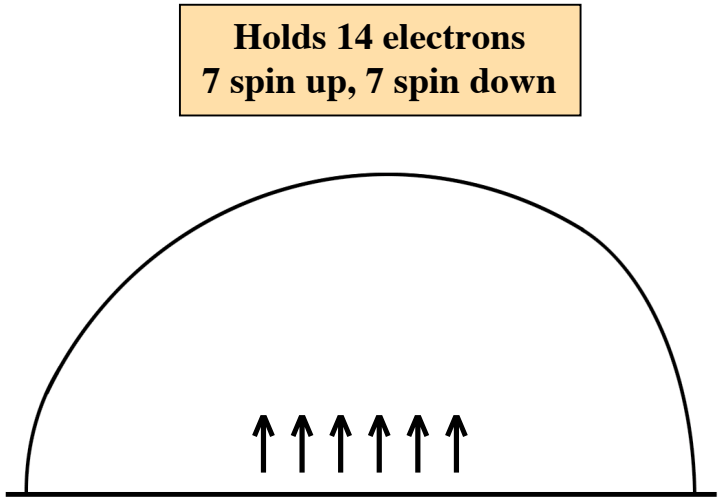
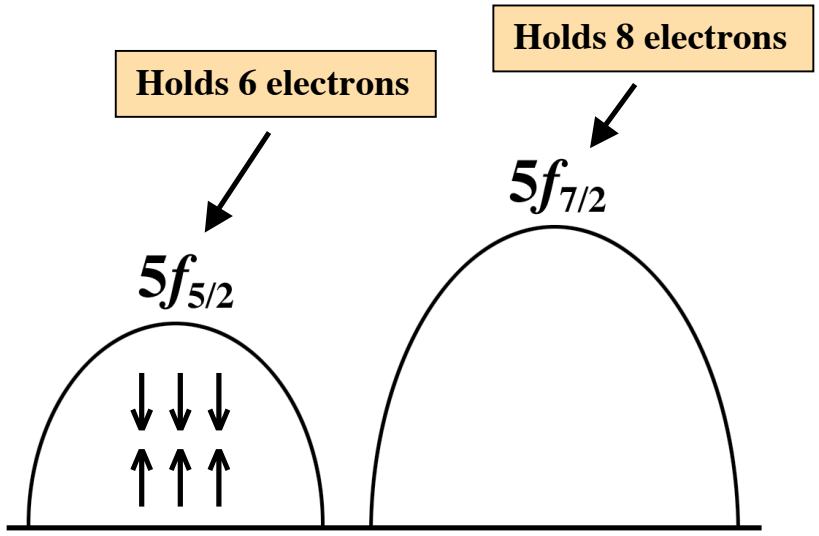


Magnetic

jj

spin-spin < orbit-orbit < spin-orbit



Non-Magnetic

We need a way to quantitatively measure where the electron are in the 5*f* states!

We have pioneered Transmission Electron Microscopy (TEM) as a quantitative solid-state physics tool for actinide science

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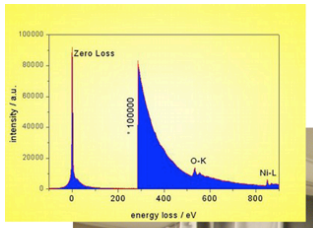
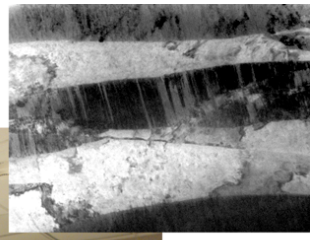
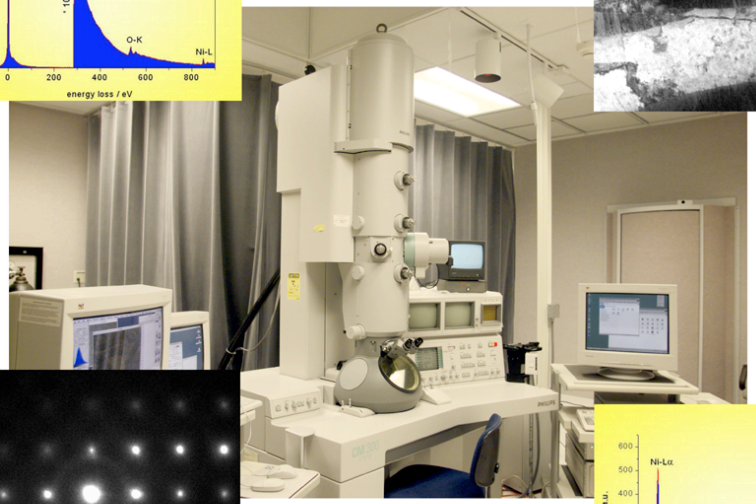
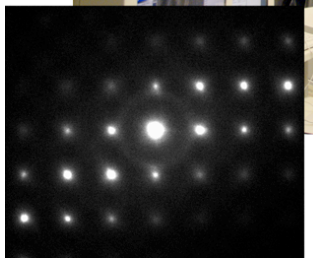
Electron Energy-Loss Spectroscopy



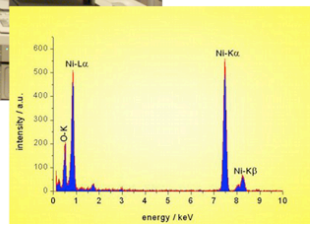


Bright-field Imaging

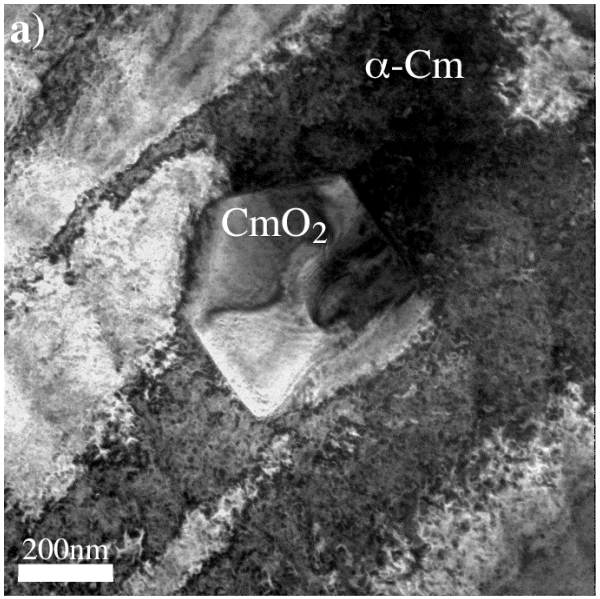




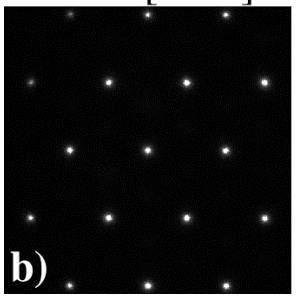
Electron Diffraction



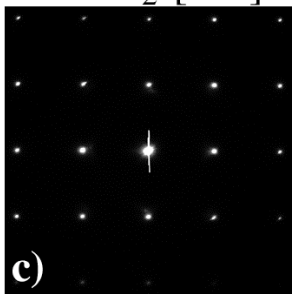
Energy Dispersive X-ray Spectroscopy



α-Cm [0001]



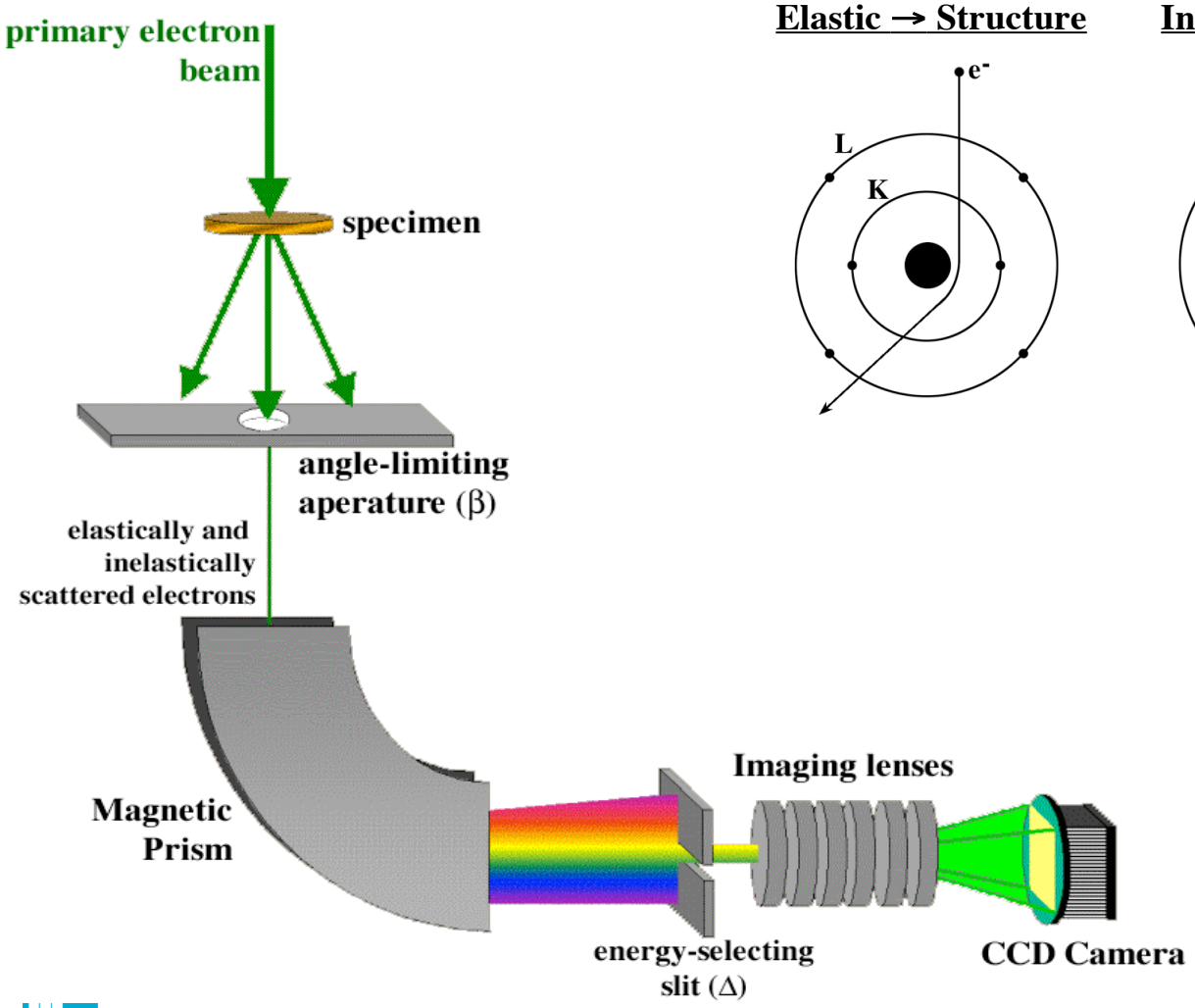
CmO_2 [001]

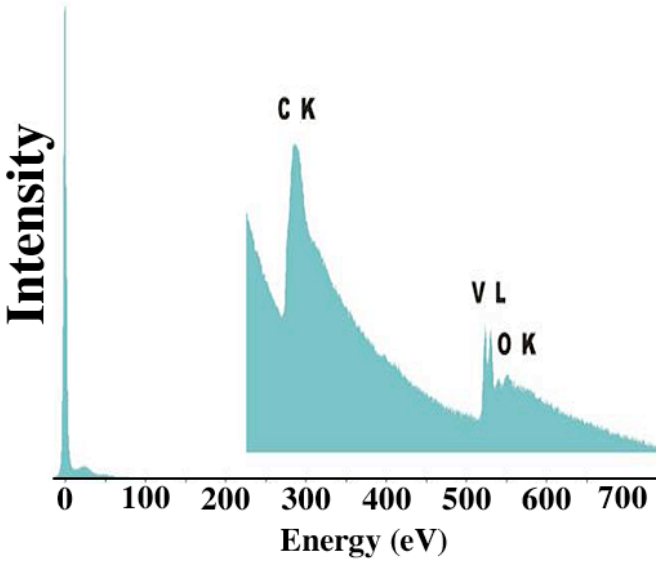


TEM provides high spatial resolution

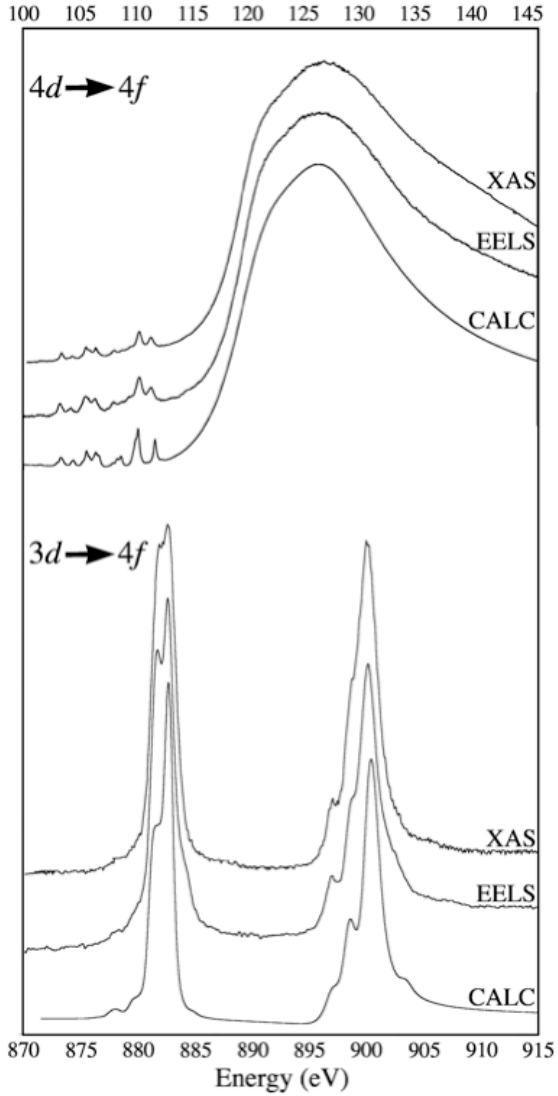
Using a 5Å electron beam, we can examine the atomic and electronic structure of phase-specific regions of a sample.

Electron Energy-Loss Spectroscopy (EELS) can be used to study the 5*f* states of the actinides





EELS in a field-emission TEM is identical to synchrotron-radiation-based XAS



K.T. Moore *et al.*, *Phil. Mag.*, **84**, 2004.

EELS versus XAS

$$\langle f | \hat{o} | i \rangle$$

↑ Matrix operator

XAS: $\hat{o} = \hat{q}\vec{r}$

EELS: $\hat{o} = \hat{q}_1\vec{r}_1 + \hat{q}_2\vec{r}_2 + \hat{q}_3\vec{r}_3 \ldots$

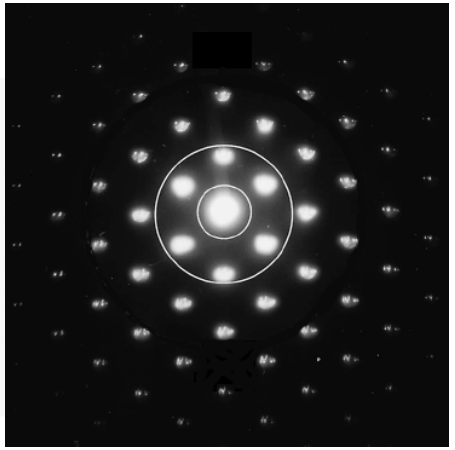
In EELS the is a quadrupole transition due to a momentum transfer

↓

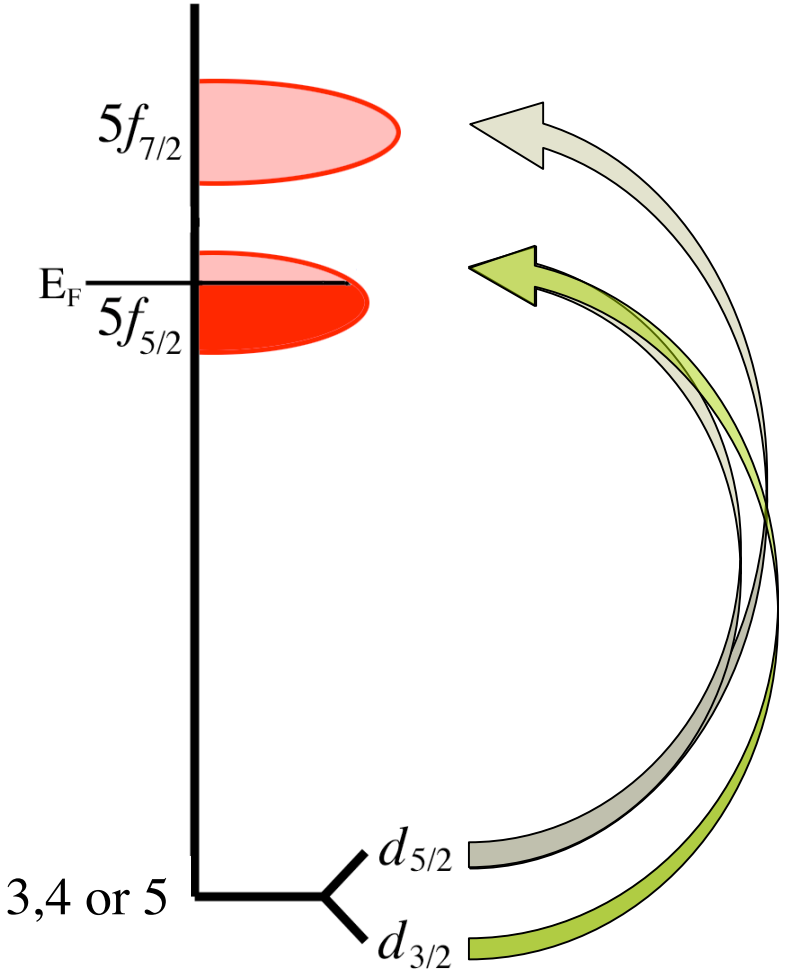
However…

↓

When a small objective aperture is employed and the primary energy of the electron beam is high (300 kV), the electron transitions are dipole for low-energy transitions.



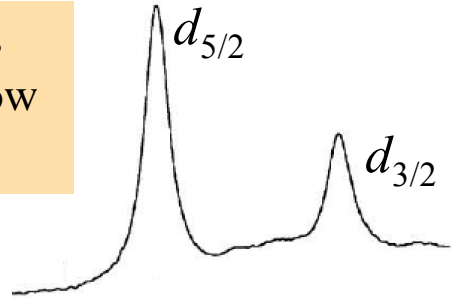
How the branching ratio of in 'white lines' of EELS spectra from actinide materials works



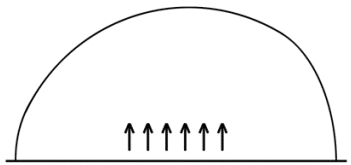
Electron dipole selection rules govern that a $d_{5/2}$ electron can be excited into either the $f_{5/2}$ and $f_{7/2}$ level.

However, a $d_{3/2}$ electron can **only** be excited into the $f_{5/2}$ level.

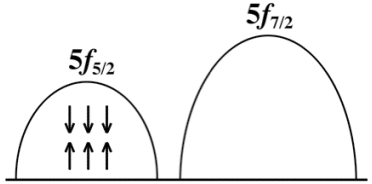
Thus, the $d_{3/2}$ and $d_{5/2}$ peaks reveal information about how the $5f$ states fill.



LS



jj

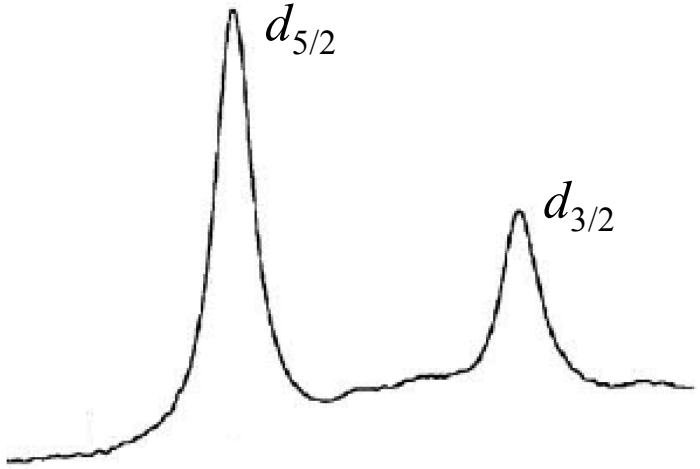


The nuts and bolts of the branching ratio and spin-orbit analysis of EELS spectra

The branching ratio of the EELS spectra is:

$$B = \frac{A_{5/2}}{\left[A_{5/2} + A_{3/2}\right]}$$

where $A_{5/2}$ and $A_{3/2}$ are the areas under the $d_{5/2}$ and $d_{3/2}$ peaks in the EELS spectra.



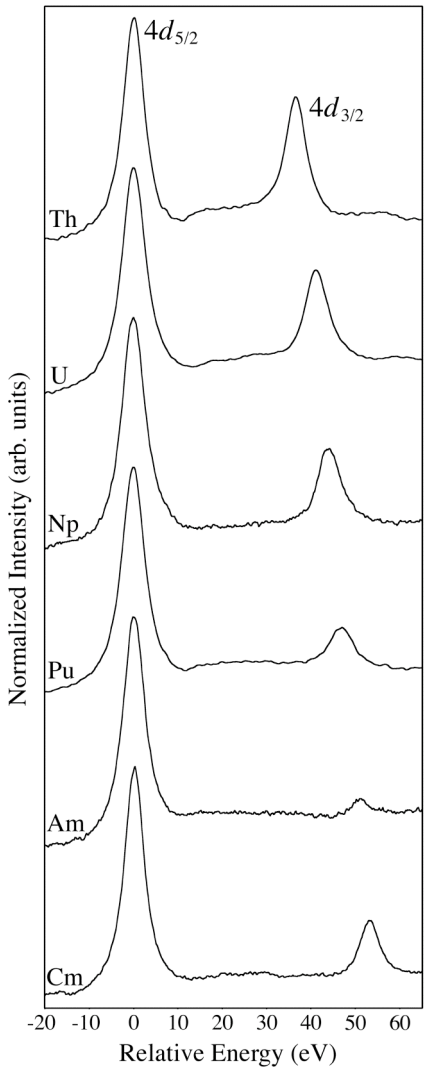
For the *f* shell, the expectation value of the angular part of the spin-orbit parameter is $\mathbf{\langle w^{110} \rangle = 2/3 \langle l \cdot s \rangle = n_{7/2} - 4/3\ n_{5/2}}$, where $n_{7/2}$ and $n_{5/2}$ are the electron occupation numbers for the angular-momentum levels j = 7/2 and 5/2.

Thus, <w110> reveals the angular momentum coupling scheme for a given material.
For the $d \rightarrow f$ transition, the sum rule gives the spin-orbit interaction per hole as:

$$\frac{\left\langle w^{110} \right\rangle}{n-14} - \Delta = -\frac{5}{2}\left(B - \frac{3}{5}\right)$$

van der Laan and Thole *Phys. Rev B*, **53**, 1996;
van der Laan *et al., Phys. Rev Lett.*, **93**, 2004.

The results: EELS spectra, branching ratio and spin-orbit analysis



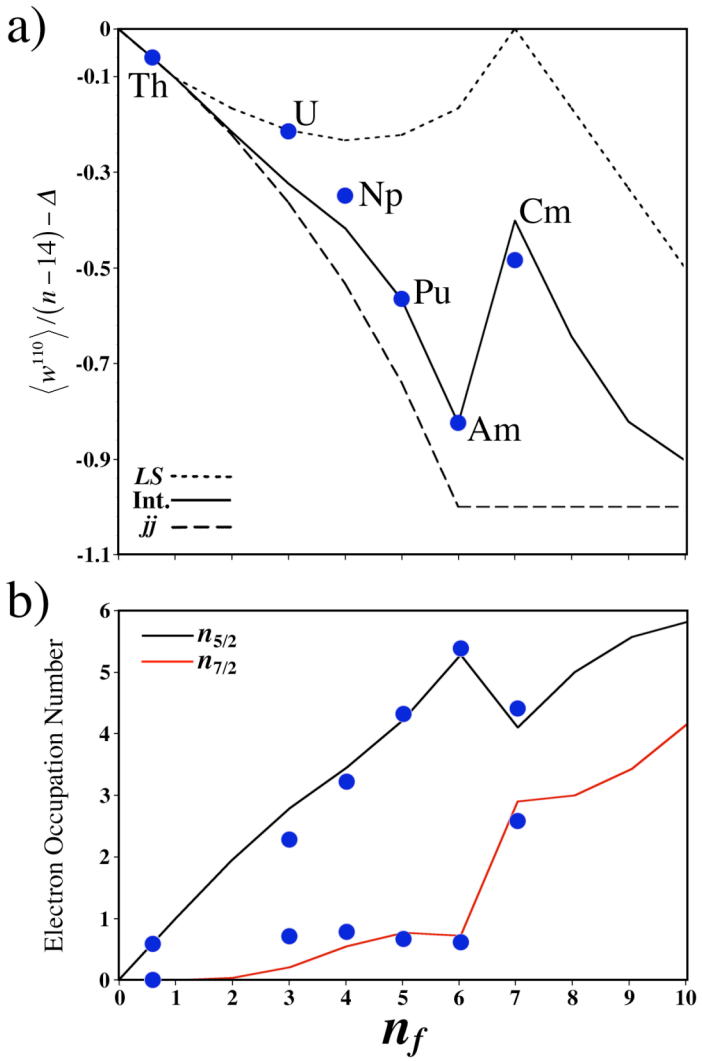
- Splitting between $4d_{3/2}$ and $4d_{3/2}$ grows with Z.
- $4d_{3/2}$ peak reduces in intensity up to Am, then increases for Cm.

$$B = \frac{A_{5/2}}{[A_{5/2} + A_{3/2}]} \qquad \frac{\langle w^{110} \rangle}{n-14} - \Delta = -\frac{5}{2}\left(B - \frac{3}{5}\right)$$

Metal	n_f	Branching ratio	$\langle w^{110} \rangle/(14-n_f)-\Delta$	$n_{5/2}$	$n_{7/2}$
Th	0.6	0.646 (003)	-0.115 (008)	0.59	0.01
U	3	0.686 (002)	-0.215 (005)	2.28	0.71
Np	4	0.740 (005)	-0.350 (013)	3.22	0.78
Pu	5	0.826 (010)	-0.565 (025)	4.32	0.67
Am	6	0.930 (005)	-0.830 (013)	5.38	0.62
Cm	7	0.794 (003)	-0.485 (008)	4.41	2.59

Moore and van der Laan, *Phys. Rev. B,* **76**, 2007.

The results of our EELS analysis on the filling of the 5*f* levels shows a large change in the coupling mechanism at Cm



What the spin-orbit analysis shows:

- Th works with all coupling - entanglement
- U exhibits LS coupling.
- Np falls in the middle.
- Pu, Am and Cm are intermediate.
- Pu and Am are near *jj*.
- Cm is strongly shifted towards *LS*.

Using spin-orbit sum rule analysis we can extract the $5f_{5/2}$ and $5f_{7/2}$ electron occupations.

$$\langle w^{110} \rangle = n_{7/2} - 4/3\ n_{5/2}$$
$$n_f = n_{7/2} + n_{5/2}$$

- Th to Am show strong filling of the $5f_{5/2}$ level.
- Not one, but TWO electrons go into the $5f_{7/2}$ level of Cm!

Moore *et al.*, *Phys. Rev. Lett.*, **98**, 2007; *Phys. Rev. B*, **76**, 2007

The abrupt change in the behavior of the 5*f* electrons at Cm is caused by *exchange interaction*

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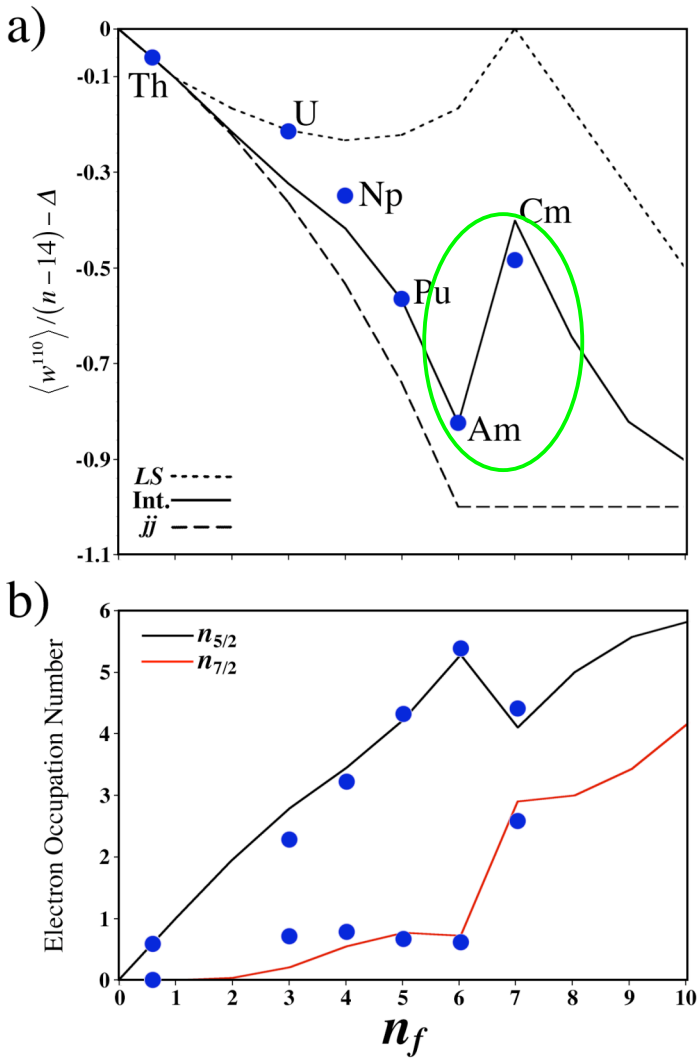
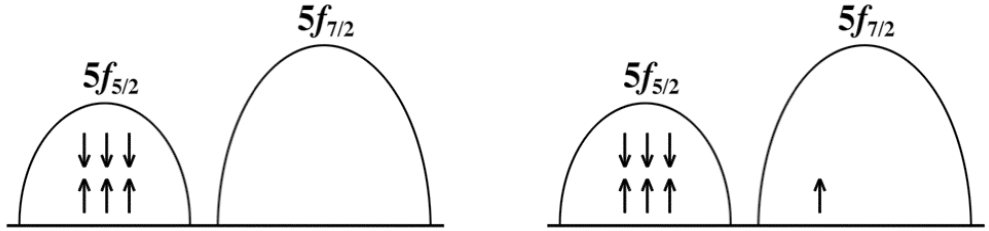


jj coupling: The electrons first fill the $f_{5/2}$ level, which can hold no more than six, then $f_{7/2}$. The maximal energy gain is thus obtained for Am f^6, since the $f_{5/2}$ level is filled.

Cm f^7 must have one electron relegated to the $f_{7/2}$ level.

The f^7 configuration has the maximal energy stabilization due to the exchange interaction, with all spins parallel in the half filled shell, and this can only be achieved in *LS* coupling.

Large change observed at Cm is due to this transition from optimal spin-orbit stabilization for f^6 to optimal exchange interaction stabilization for f^7.



Stable **Unstable**

Moore *et al.*, *Phys. Rev. Lett.*, **98**, 2007; *Phys. Rev. B*, **76**, 2007

We explain the magnetic stabilization of curium by calculated magnetic moments in different coupling mechanisms.

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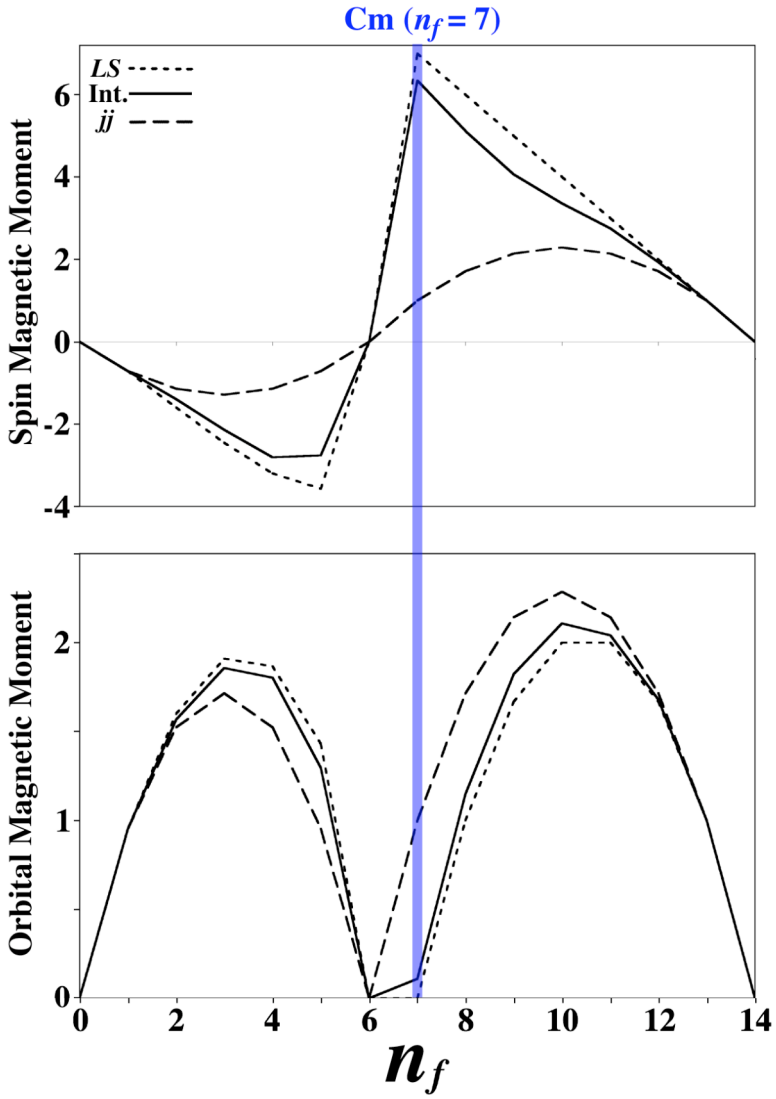
The choice of coupling mechanism plays a large influence on the spin and orbital magnetic moments.

This is most remarkable for Cm: Spin moment is modest for *jj*, but is large for *LS* and intermediate.

Thus, the large shift towards *LS* coupling produces the strong spin polarization that stabilized curium!

Our results explain the magnetic stabilization observed by Heathman *et al.*, Science (2005).



Moore *et al.*, *Phys. Rev. Lett.*, **98**, 2007

Density-functional theory shows how important spin polarization is to all five pressure-induced phases of curium

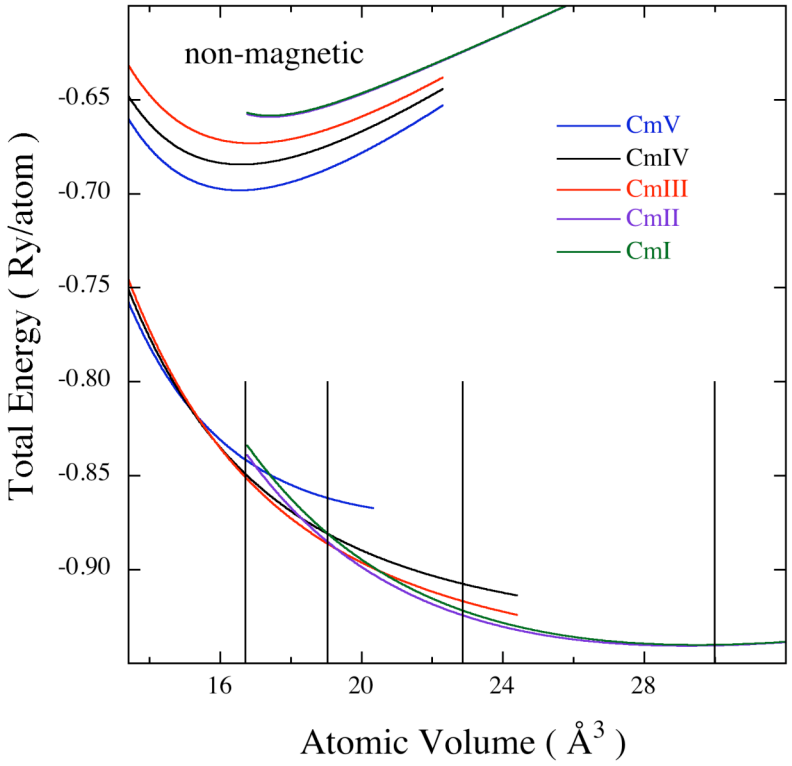


TABLE II. The spin, orbital, and total moments, m_s, m_l and m_{total} (in μ_B) for Cm I-V as calculated by DFT.

Cm phase	Volume (Å^3)	m_s	m_l	m_{total}
I	30	6.6	0.4	7.0
II	22.8	6.16	0.35	6.51
III	18.9	5.43	0.38	5.81
IV	16.7	4.57	0.59	5.16
V	13.7	0	0	0

Moore *et al.*, *Phys. Rev. Lett.*, **98**, 2007

Spin polarization is imperative to achieve the correct series of phases for Cm metal under pressure.

This is most true for the low-pressure phases, but becomes less so for the high-pressure phases Cm IV and V.

Very recent dynamical mean-field theory results support this view for plutonium and curium

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Dynamical mean-field theory (DMFT) results in relation to ours:

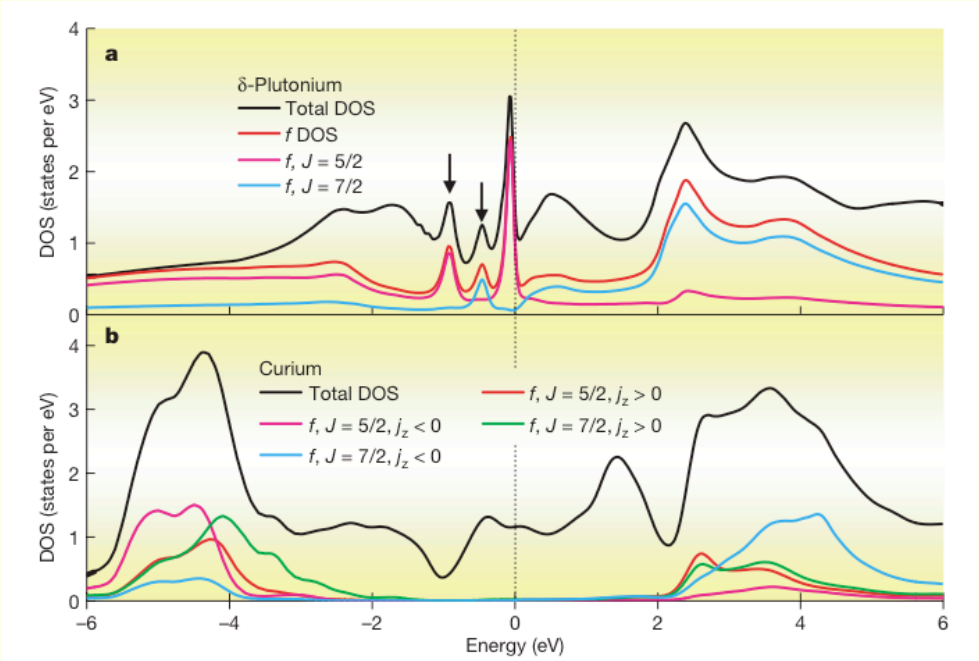

Table 1 | Branching ratio

	f count	$B_{DMFT\ theory}$	B_{exp} (ref. 16)	B_{L-S}	B_{jj}	$(B_{DMFT} - B_{L-S})/(B_{jj} - B_{LS})$
δ-Plutonium	5.2	0.83	0.847	0.69	0.90	0.67
Curium	7.0	0.75		0.6	1.0	0.38

The *f*-electron count and branching ratio, *B*, of the $4d \rightarrow 5f$ edge spectra of δ-plutonium and curium. B_{L-S} and B_{jj} correspond to limiting cases of the pure Russell-Saunders and *j*–*j* coupling, respectively.

Shim *et al.*, *Nature* **446**, 2007.

The results of Shim *et al.* show:

Density of States:

- Close to experiment for Pu (Havela *et al.*, PRB, 2005).
- As expected for Cm.

Shim *et al.* then calculate what the branching ratio and S-O interaction would be for each metal….

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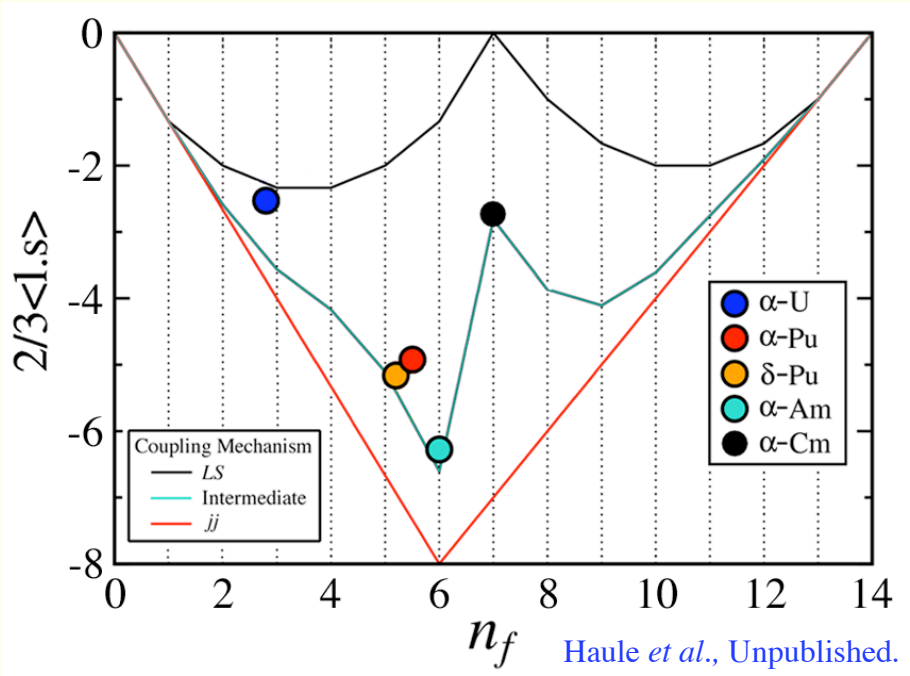


Haule *et al.*, Unpublished.

Table 1 | Branching ratio

	f count	$B_{DMFT\ theory}$	B_{exp} (ref. 16)	B_{L-S}	B_{jj}	$(B_{DMFT} - B_{L-S})/(B_{jj} - B_{LS})$
δ-Plutonium	5.2	0.83	0.847	0.69	0.90	0.67
Curium	7.0	0.75		0.6	1.0	0.38

The *f*-electron count and branching ratio, *B*, of the $4d \rightarrow 5f$ edge spectra of δ-plutonium and curium. B_{L-S} and B_{jj} correspond to limiting cases of the pure Russell-Saunders and *j*–*j* coupling, respectively.

Shim *et al.*, *Nature* **446**, 2007.

The results of Shim *et al.* show:

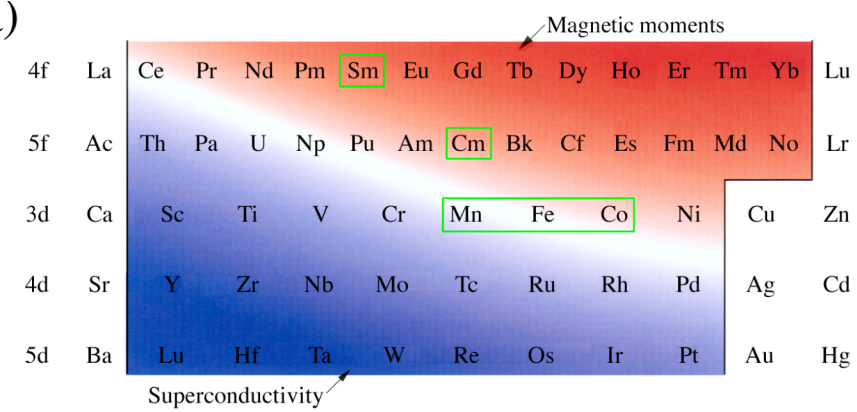
- Intermediate coupling near the *jj* limit for Pu and Am.
- Intermediate coupling near the *LS* limit for Cm.

Thus, DMFT shows the large jump in the spin-orbit expectation value between Am and Cm, just as our atomic and EELS results!

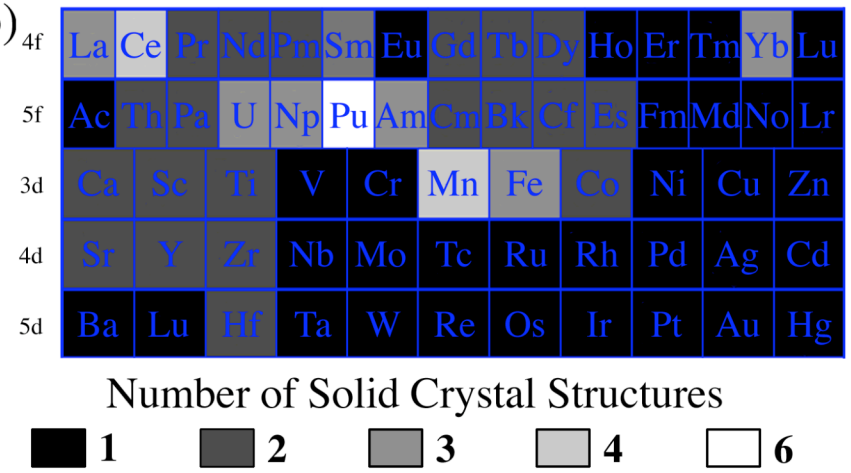
The Big Picture: Magnetic stabilization of metals throughout the Periodic Table

cmls Directorate

a)



b)



The atomic crystal structure of some metals is influenced by the element's own intrinsic magnetism, meaning polarization of bonding electrons dictates atomic geometry.

Green boxes show metals with crystals structures known to be stabilized by magnetism: Mn, Fe, Co, Sm and Cm.

The determining factors for magnetic stabilization of metallic crystal structures:

1) Proximity of the element to the border between super-conducting and magnetic valence electron behavior (small energy difference between crystals).

2) Presence of strong intrinsic magnetism.

The Big Picture: Magnetic stabilization of metals through the Periodic Table

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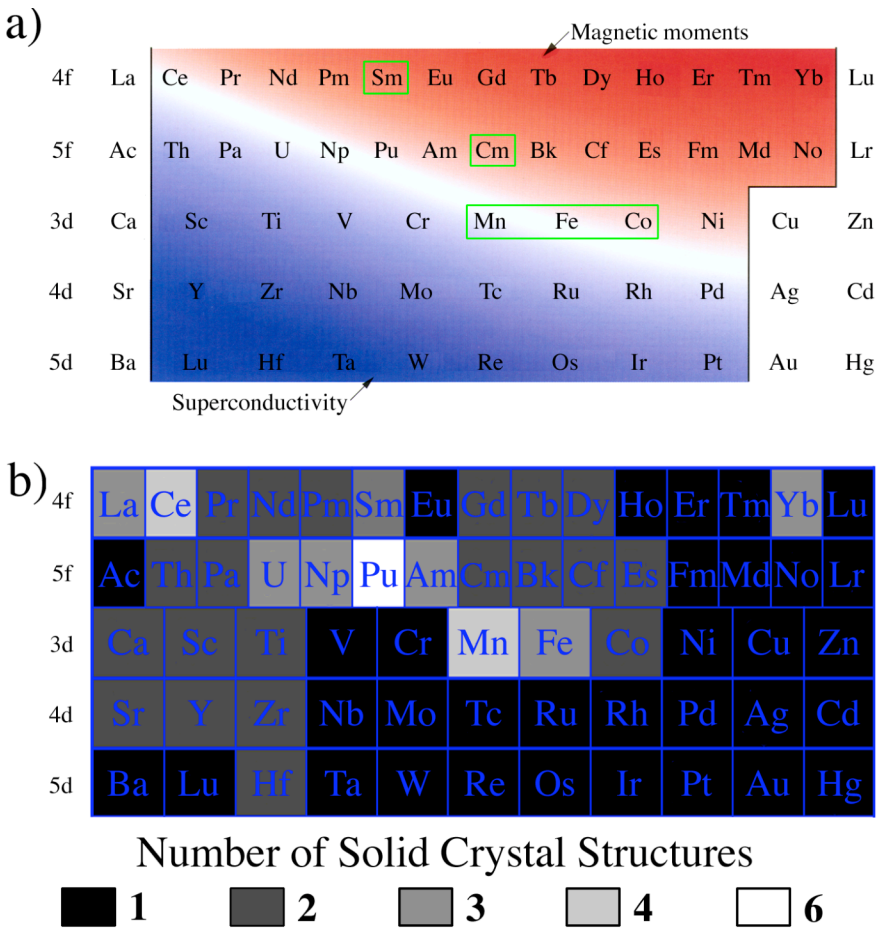

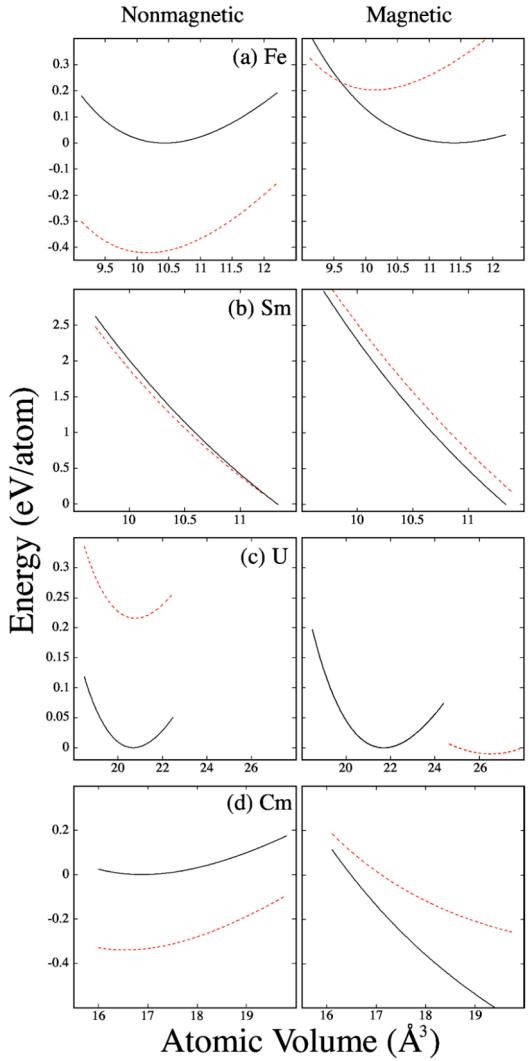

Söderlind and Moore, *Phys. Rev. Lett.*, in review.

The Big Picture: Magnetic stabilization of metals through the Periodic Table

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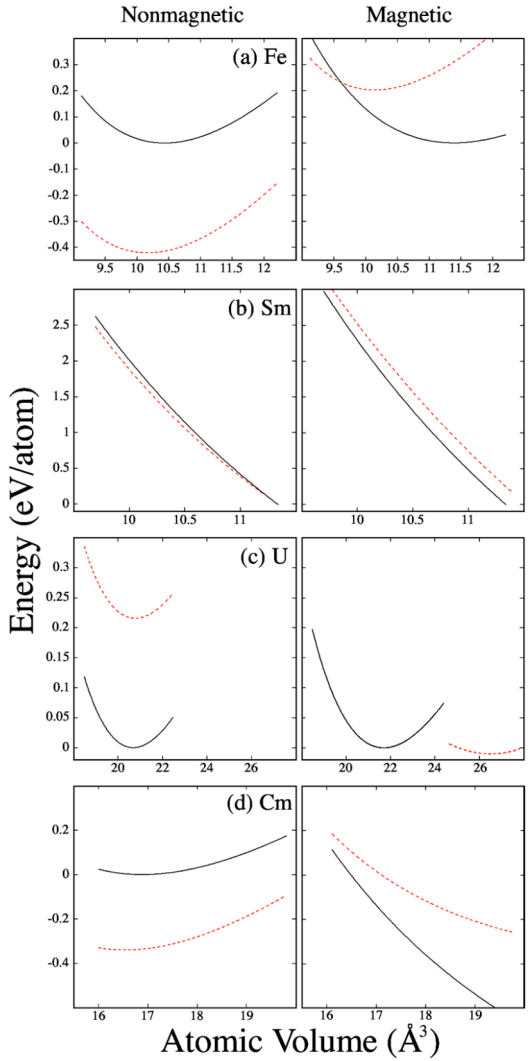
Metals on or near the itinerant-localized transition have crystal structures that are easily altered by magnetism.

In contrast, the 4*d* metal Ru is located to the left of the itinerant-localized transition and does not have a magnetically stabilized crystal structure. Ru is also extraordinarily stable in its non-magnetic (hcp) ground-state phase.

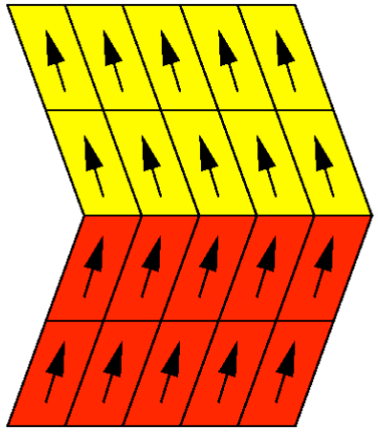
Indeed, our calculations suggest no magnetic state in Ru even when subjected to gigantic external fields (~ 10000 Tesla).

In other words, magnetism - intrinsic or external - does not alter the crystal structure of Ru.



Söderlind and Moore, *Phys. Rev. Lett.*, in review.

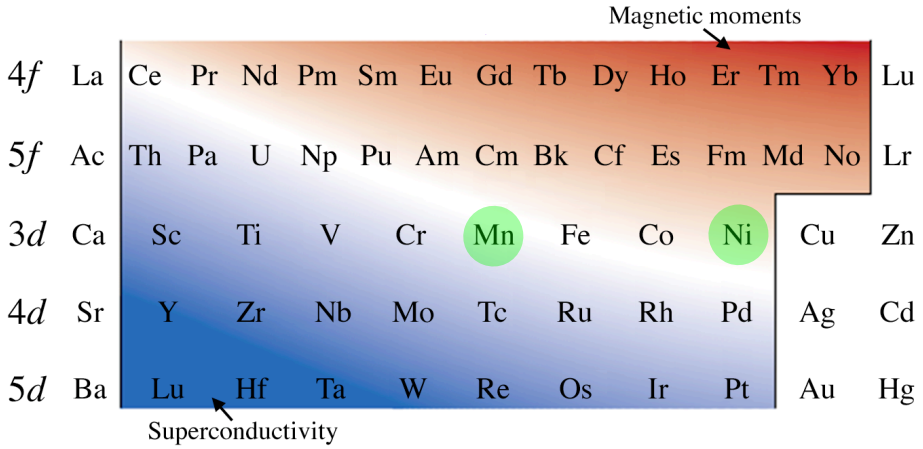
Ni-Mn-Ga: Example of engineered material with magnetic applications



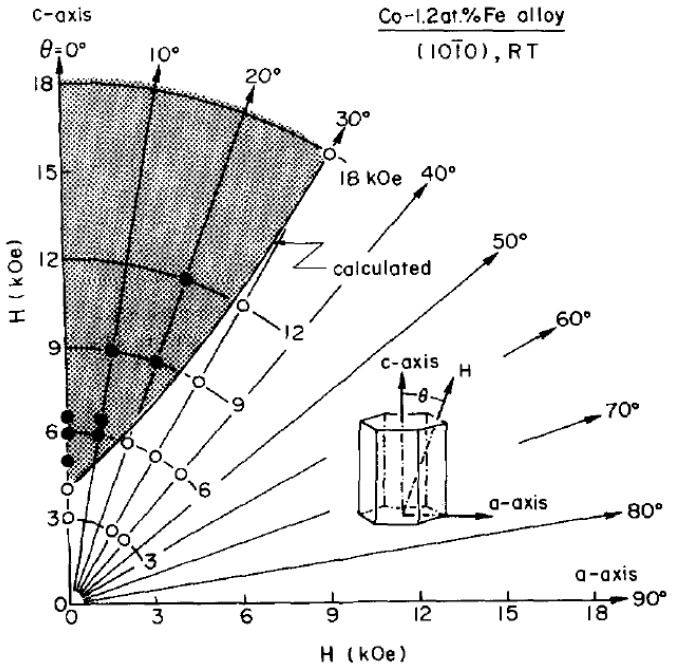
Boonyongmaneerat *et al.*, *Phys. Rev. Lett.*, 2008.

Sonar, precision valves, etc. use materials that change shape when exposed to a magnetic field.

Magnetic shape-memory materials come from a magnetically sensitive atomic structure.

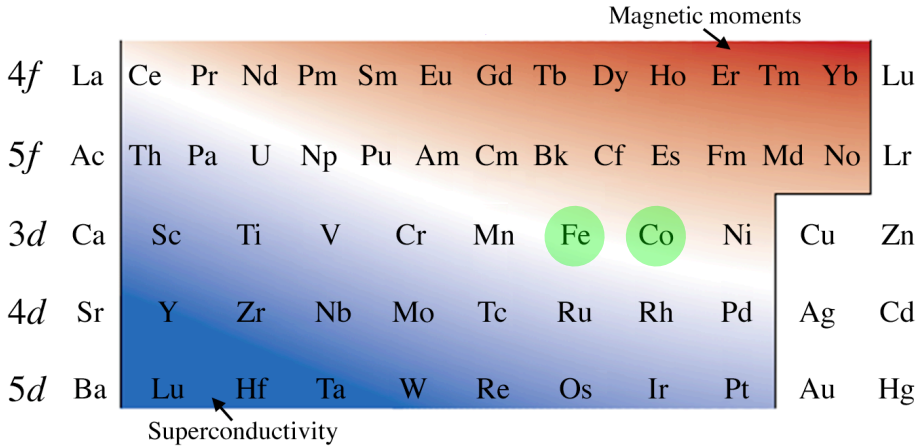


Co-1.2at.%Fe alloy: Example of engineered material with magnetic applications



Tanaka *et al.*, *J. Mag. Mag.* Mater., 1983.

When Co-1.2at.%Fe is exposed to a magnetic field of 0.5 Tesla or more within 20° to parallel of the *c* axis a field-induced dhcp → hcp transformation occurs.



Conclusions:

1) The 5*f* electrons in Cm are near an *LS* coupling scheme.

2) This coupling scheme allows for a large spin polarization of the 5*f* electrons, which in turn stabilizes the Cm III crystal structure.

3) Results for Cm show us the recipe for magnetic stabilization of the crystal structure of metals:
   - A) The metal must be near the itinerant-localized transition where multiple crystal structures have close energies.
   - B) The metal is just on the magnetic side of the transition.
   - C) There must be a magnetic moment large enough to overcome the energy difference between crystal structures, thus dictating the atomic geometry.

4) These results solidify our understanding of magnetically-stabilized metals, showing us where to look for engineered materials with magnetic applications.